Kinetics of DTPA extraction of zinc from calcareous soils from Iran

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Abstract

In recent years, our knowledge of Zn extraction from soil has been based mainly on the study of equilibrium condition using thermodynamic approaches. Thermodynamics can predict only the final state, while a knowledge of desorption kinetics may yield important information concerning the nature of reactions and also the rate of supply of Zn to plants via soil solution. The kinetics of Zn extraction by diethylenetriaminepentaacetic acid (DTPA) from the -2mm fraction of 12 calcareous soils was investigated using surface soil (0-30 cm) samples. Soils were equilibrated with 0.005 M, DTPA solution for 15 to 11520 minutes. Zero-, first-, second-, third order, parabolic diffusion and simple Elovich equations did not adequately describe Zn extraction kinetics. The best model for describing extraction data for all soils was the exponential rate equation ($q = a\ t^b$). The magnitude constant, a, was significantly and positively correlated ($r = 0.76$) to organic carbon content and negatively correlated to pH ($r = -0.67$). The rate constant, b, was not significantly related to any of the measured soil properties (pH, CEC, CCE, ACCE, clay, OC, SSA) or to any combination of properties. It was concluded that the amount of Zn that can be extracted by DTPA solution from Iranian calcareous soils is highly variable.

Key Words
Aridisols, Entisols, carbonate, kinetic models.

Introduction
Considerable work has been carried out on the kinetics of extraction of P and K from soils and these findings have been related to soil properties and the availability of these elements to plants. However, investigations of the kinetic of Zn extraction from soil have been limited (Sparks *et al.* 1980; Sparks 1986; Dang *et al.* 1994) and there are no published reports on Zn extraction from calcareous soils of Iran where Zn deficiency in crops is widespread (Maftoun and Karimian 1989). Calcareous Aridisols and Entisols in Iran generally contain quite large quantities of total Zn, but have only very small quantities of Zn in soil solution. Most of these soils need supplemental Zn for optimum plant growth (Reyhanitabar *et al.* 2007) and the recovery of applied Zn by plants is low. Even where Zn chelate (Zn-EDTA) was applied only 5% or less was recovered by the first crop (Maftoun and Karimian 1989). This may reflect the rapid formation of Ca-EDTA in calcareous soils and loss of Zn from solution by sorption and precipitation.

The uptake of Zn by plants requires release of Zn sorbed on soil surfaces and possibly dissolution of Zn containing minerals (Uygur and Rimmer 2000). The rate of Zn release to soil solution is thus an important factor regulating its supply to plants. The chelating agent, DTPA is routinely used to estimate available Zn in calcareous soils (Lindsay and Cox 1985), but this standard method provides only a static or single measure of Zn availability to plants whereas dissolution of Zn in DTPA increases or decreases with time. Thus the kinetics of Zn dissolution in DTPA for different soil types need to be known so as to optimize extraction times for testing particular soil types. DTPA chelates Zn and to an extent simulates both Zn extractions from soil by plant exudates and Zn uptake by plants. The kinetic of Zn dissolution in DTPA may thus provide an indication of the rate of Zn supply to plants. This is especially important for Aridisols and Entisols, which contain considerable Zn but have very small amounts of Zn in soil solution (Maftoun and Karimian 1989). For these soils continuing Zn release from the soil over time will increase Zn availability to plants. Zinc extraction kinetics was investigated by Kuo and Mikkelsen (1980) and these data were described by an exponential rate equation. However other equations have been proposal for describing extraction kinetics and these may provide better descriptions of Zn extraction from soil (Sparks 1986). This study has determined the kinetics of Zn extraction by DTPA for 12 Aridisols and Entisols from Iran and identifies the equations that best describe this process.

Methods
Twenty composite soil samples (0-30cm) from the Gazvin Plains and Tehran province (Iran) were collected. Soil samples were air dried, ground in a stainless steel mill to pass a 2 mm sieve, stored in airtight polyethylene containers, and analyzed by the following procedures: Identification of carbonates and clay minerals was carried out by X- ray diffraction (XRD) using random powder and oriented clay on ceramic plates with a Philips PW 1830/40 instrument. Specific surface area (SSA) was measured using the N2-BET method with a Micrometrics Gemini III 2375 surface area analyzer.

To measure Zn extraction 50g oven-dried soil was extracted in duplicate with 100 ml of a solution consisting of 0.005 M Diethylentriaminepentacetic, 0.1 M triethanolamine, and 0.01 M $CaCl_2$ at pH 7.3 (Lindsay and Norvell 1978) at 25˚C ±1 in a constant temperature shaker, for periods of 0.25, 0.5, 1, 2, 4, 8, 12, 24, 36, 48, 60, 72, 96, 120, 144, 168 and 192 hours. Seven drops of toluene were added to each flask to inhibit microbial activity. For each shaking period, a 5 mL subsample of the suspension was removed with a plastic syringe and the suspension was filtered through a 0.45 μm filter. Zinc concentration was determined by ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) using a Perkin–Elmer Elan instrument.

Kinetic equations that have been used in soil extraction studies, namely zero-, first-, second- and third order rate equations (Dang *et al*. 1994), parabolic diffusion, exponential and Elovich (Khater and Zaghloul 2002) were evaluated by least- squares regression analysis for their suitability for describing Zn extraction data. A relatively high value of the coefficient of determination (r^2) was used as the criterion for the best fit.

Results and Discussion
Soil characteristics
In the studied soils, clay concentrations range from 106 to 410 g/kg, pH ($CaCl_2$) from 7.2 to 7.8, organic carbon from 6.3 to 24.7 g/kg, SSA from 8.5 to 39 m²/g. Calcium carbonate equivalent ranged from 46.0 to 228.0 g/kg and active $CaCO_3$ equivalent ranged from 16.1 to 99.8 g/kg. DTPA extractable Zn values ranged from 1.2 to 4.9 mg/kg. X-ray diffraction (XRD) analysis of random powders identified abundant quartz and showed that calcite is the sole carbonate mineral. X-ray diffraction patterns of the clay fraction identified illite, chlorite and smectite as major clay minerals in all soil samples.

Kinetics of Zinc Extraction
Extraction of Zn in DTPA from 12 Aridisols and Entisols increased with time and the amount of Zn extracted differed greatly among soils (Figure1).
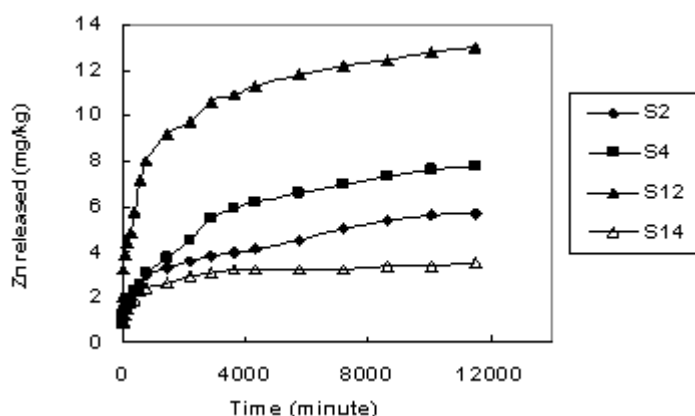

Figure 1. Zinc extracted by DTPA for some calcareous soils.

The amount of Zn extracted at 192h was approximately three fold higher for soil 2 (loam) compared to soil 14 (clay). Similar results have been reported by Dang *et al*. (1994) for Zn extraction by DTPA from vertisols. The zero-, first-, second-, and third- order, parabolic diffusion, Elovich and exponential equation were evaluated for describing Zn extraction kinetics up to 192h. The extraction kinetic was poorly described by the zero-, first-, second-, and third-order equations. With the increasing order of reaction from zero to third, the coefficient of determination (r^2) decreased for all soils which are consistent with the findings of Dang *et al*. (1994). These models fail to adequately describe Zn extraction kinetics and will not be discussed further. The parabolic diffusion equation provides an adequate description of extraction kinetics based on r^2, but there were systematic departures of data from the fitted curves .There was a discontinuity in the slope of the

fitted line at about 24h suggesting that two different mechanisms with different rate constants are controlling the net rate of Zn extraction. For 9 of 12 soils, there are significant differences between the two linear slopes with the first slope (< 24h) being higher than the second slope. Parabolic diffusion equations have been fitted to the two sections of extraction data and provide an excellent fit to the data (r^2=0.98). As film diffusion was minimized by continuous shaking during the experiment (Sparks *et al*. 1980) it is likely that at least two particle diffusion mechanisms were involved. Possibly Zn was mostly desorbed from outer surfaces of micro-aggregates in the first 24h, with subsequent dissolved Zn being mostly provided by desorption and diffusion of Zn from inside aggregates (Figure2). This explanation is consistent with the Zn diffusion model of Bruemmer *et al*. (1988), the Zn sorption model of Barrow (1986) and the findings of Dang *et al*. (1994) for Vertisols, although Dang *et al*. (1994) reported a discontinuity in slope after very short extraction time. Extraction kinetics were well described by both exponential and Elovich equations although there were small systematic departures of data from the relationships in both cases (Figure3). The exponential equation provided higher values of r^2 than the Elovich equation. The values of constants "a" and "b" vary widely for different soil types. In this study "a" ranged from 0.35 to 1.32 with a mean of 0.69 and b from 0.19 to 0.33 with a mean of 0.25. The values of "a" for these calcareous Iranian Aridisols and Entisols are much higher than values for vertisols, reported by Dang *et al.* (1994) but the "b" values are similar. The constant "a" was positively correlated with organic carbon content, and negatively with pH. There was no significant relationship between rate constant b and measured soil properties either singly or in combination. Constant ,a, may indicate the number of surface sites available for desorption of Zn i.e. the total desorable Zn. Constant ,b, is a measure of the affinity of Zn for thses sites with increasing affinity of sites being indicated by the value of 1/b.
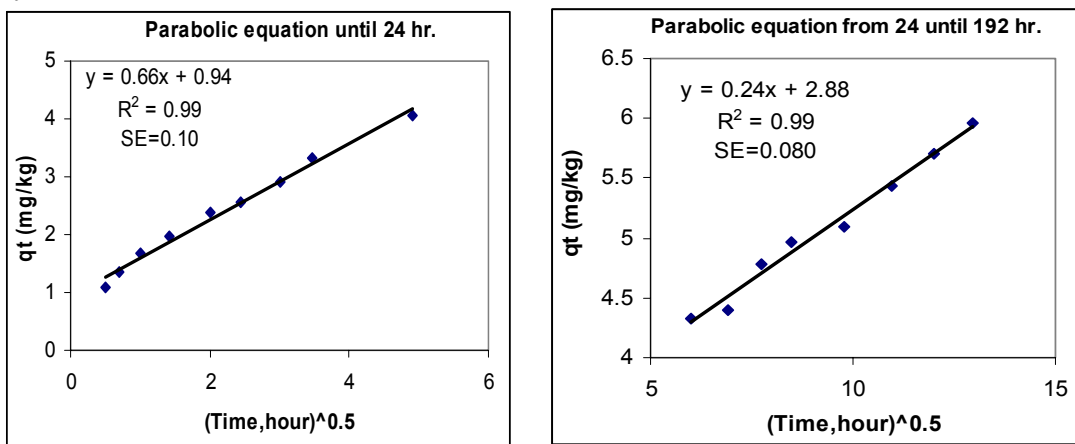

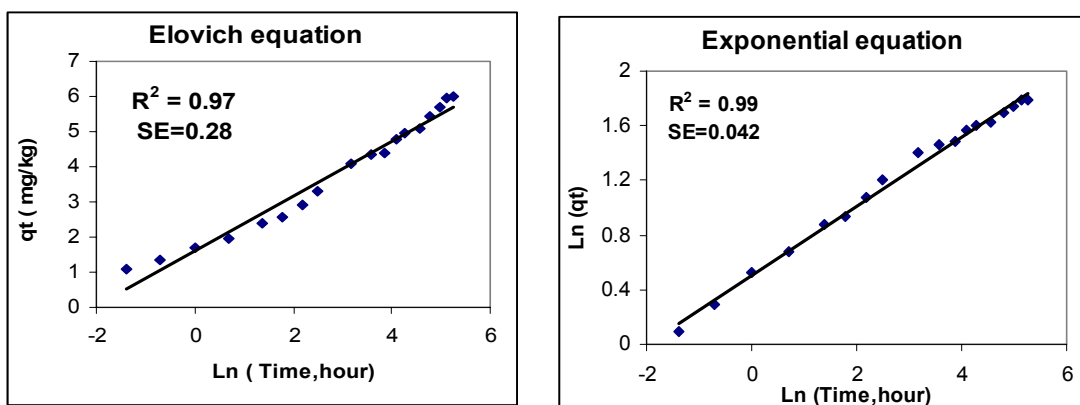Figure 2. Zinc extracted data fitted to the parabolic equation for two periods for soil 5.

Figure 3. Fitted zinc extracted data for a calcareous soil (#5) according to the Elovich and exponential equations.

Conclusions

This research has shown that the amount of Zn that can be extracted by DTPA solution from Iranian calcareous soils is highly variable. The amount of extractable Zn for long extraction times (a constant) increases with the organic matter content of the soil and decreases as soil pH increases. This association with organic matter has also been observed by previous authors (Brennan 1992; Dabkowska 2003). The rate at

which Zn was extracted from the soil (related to the b constant) was quite variable and is not systematically related to any of the measured soil properties. Consequently a soil test for available Zn that involved extraction for a single quite short time period may underestimate the amount of Zn that is eventually released to soil solution and plants. This research would have been fitted by inclusion of plant growth and Zn uptake measurements to calibrate the results of DTPA extraction and in particular to evaluate if the "a" and "b" constants can be utilized for predicting Zn uptake by plants. On this basis a soil type specific extraction procedure could be developed.

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